TECHNICAL MEMORANDUM

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CHLORINE AND CHLORINE DIOXIDE
DOMTAR AND C.I.L.
CORNWALL, ONTARIO
SEPTEMBER, 1986

ARB-216-86-AQM

February, 1987

Ministry of the Environment
Ontario

E. PICHÉ, Director
Air Resources Branch

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- prepared for -

The Southeastern Region
Ontario Ministry of the Environment

- prepared by -

Gary B. DeBrou
Senior Project Scientist
Air Resources Branch

February, 1987

EXECUTIVE SUMMARY

In response to a request presented by the Southeastern Region, the mobile TAGA unit of the Ministry's Air Resources Branch conducted an intensive air monitoring survey in Cornwall, Ontario during the first three weeks of September, 1986. The survey objective was to determine ambient levels of chlorine (Cl_2) and chlorine dioxide (ClO_2) in the vicinity of Domtar Fine Papers and Chemical Industries Limited (C.I.L.)

As in previous surveys, it was found that C.I.L. was not a source of detectable levels of airborne Cl_2 and ClO_2. For all seven ½-hour monitoring periods the average concentrations of Cl_2 and ClO_2 were below the analytical detection levels of 1 ug/m^3 for Cl_2 and 0.2 ug/m^3 for ClO_2. Thus, the Cl_2 and ClO_2 levels downwind of C.I.L. were orders of magnitude below the Ministry standards of 300 ug/m^3 and 85 ug/m^3 for Cl_2 and ClO_2 respectively.

On-site TAGA measurements of Cl_2 and ClO_2 acquired downwind of Domtar indicated the presence of Cl_2 and ClO_2. The maximum ½-hour average of ClO_2 was 17 ug/m^3, well below the Ministry standard. In fact, a majority of ClO_2 determinations were below 1 ug/m^3. The ½-hour average concentrations of Cl_2 range from 4.4 to 840 ug/m^3, with 10 of the 37 ½-hour sampling periods indicating the Cl_2 levels downwind of Domtar to be in exceedance of the Ministry standard of 300 ug/m^3. Relatively high levels of Cl_2 coincided with the detection of sulfurous and chlorine odours.

1.0 Introduction

As requested by the Southeastern Region of the Ontario Ministry of the Environment, the mobile TAGA unit of the Air Resources Branch conducted an air monitoring survey in Cornwall, Ontario, during September, 1986. The objective of the survey was to determine ambient levels of chlorine (Cl_2) and chlorine dioxide (ClO_2) in the vicinity of Domtar and C.I.L. Reported here are the findings of the three week survey and the TAGA monitoring techniques for Cl_2 and ClO_2.

2.0 The Mobile TAGA

The mobile TAGA system represents the state-of-the-art in ambient air analyses. It is a self-contained mobile laboratory capable of monitoring a variety of airborne pollutants at ultra trace levels in the real-time. Past applications have included chlorine monitoring at two pulp and paper mills, a sodium chlorate plant, and the well-publicized Mississauga derailment.

The TAGA, or Trace Atmospheric Gas Analyzer, is a specialized quadrupole mass spectrometer with a unique sampling inlet system and ion source which operates at atmospheric pressure. The unique features of the TAGA system allow ambient air to be sampled directly into the ionization chamber for rapid mass spectral analysis. The mobile TAGA has proven to be invaluable for the tracking of pollutant plumes to their source of origin.

An important aspect of any ambient air measurement is the knowledge of local meteorological conditions. Thus, the mobile TAGA is equipped to monitor wind speeds, wind directions and ambient temperatures simultaneously with the acquisition of air quality data.

The operation of the TAGA, and the acquisition of the meteorological and air quality data are under strict computer control. Instantaneous concentrations of pre-selected pollutants are continually updated on the CRT screen, allowing the survey scientist to access the monitoring results in the field and subsequently formulate an effective survey strategy.

2.1 Survey Strategy

Basically the survey strategy was to position the mobile TAGA unit downwind of Domtar and/or C.I.L., and acquire instantaneous concentrations of ambient Cl_2 and ClO_2. Monitoring locations were selected using the following criteria, in order of importance:

1) prevailing wind directions;
2) road network and accessibility;
3) plume tracking results; and
4) presence of odours.

Wind speed and wind direction data, collected at a height of 10 meters, were displayed by the on-board computer system and updated every 30 seconds. The meteorological data ensured that the monitoring locations were indeed downwind of the source of interest. Despite the physical closeness of Domtar and C.I.L. (both located at Brookdale and Second), it was possible to determine their respective contributions of Cl_2 and ClO_2 through the careful selection of monitoring sites and appropriate winds.

Plume tracking refers to the real-time determination of target pollutant levels (e.g. Cl_2) while the TAGA unit was driven in the vicinity of the alleged source(s). Provided the meteorological conditions are more or less constant, and the

pollutant levels are above the analytical detection limits, plume tracking can quickly reveal the highest ground level concentrations and the "best" monitoring locations.

The presence of chlorine-like odours was not always a prerequisite for data collection since it is plausible that the ambient chlorine levels may be below the odour threshold limits. Furthermore, chlorine odours may be masked by other more odourous components; for instance, the reduced sulfur odour often detected downwind of Domtar.

Once a sampling site had been selected, instantaneous levels of chlorine and chlorine dioxide were recorded every 10 seconds, for a period of at least 30 minutes. The ½-hour averaged concentrations were obtained by calculating the arithmetic mean of 181 measurements acquired over a 30 minute period. Several half-hour averages were acquired at various distances from the source(s) of interest over the three week survey period.

In addition to downwind measurements, background levels of chlorine and chlorine dioxide were determined upwind of the source(s). The daily background, or upwind, signals were used to correct the downwind measurements. Note that neither Cl_2 nor ClO_2 were observed in any of the background samples.

2.2 Chlorine and Chlorine Dioxide Monitoring Techniques

Trace levels of ambient Cl_2 and ClO_2 are readily observable by the TAGA system. The TAGA, an atmospheric-pressure chemical ionization mass spectrometer (APCI/MS), produces $O_2^-.(H_2O)_n$ reagent ions which rapidly ionize Cl_2 and ClO_2, producing negative ions at m/z values of 67, 69, 70

and 72, corresponding to the ionic species: $(^{35}ClO_2)^-$, $(^{37}ClO_2)^-$, $(^{35}Cl.^{35}Cl)^-$, $(^{37}Cl.^{35}Cl)^-$. Owing to the natural isotope abundance of $^{35}Cl/^{37}Cl$ (i.e. 3/1), the theoretical ratios of masses 67/69 and 70/72 will be 3:1 and 3:2 respectively.

Thus APCI mass spectrometry is an ideal technique to quickly confirm the presence of chlorine and chlorine dioxide in the atmosphere. As well, the exceptional sensitivity of the TAGA system enables instantaneous measurements of chlorine and chlorine dioxide at levels lower than 1.0 ug/m^3. The detection limit is defined as 3 times the standard deviation of the background signal, divided by the slope of the response curve.

2.2.1 Chlorine Calibration Technique

Calibration of the TAGA for chlorine was accomplished using a dynamic flowing system. A known quantity of chlorine was fed directly into the ambient air sampling inlet system. A certified standard (Matheson) of 51.7 ppm chlorine in ultra pure nitrogen was used. Flow control was facilitated by a standard ball rotameter, which had been pre-calibrated by a soap-film technique.

During each monitoring day six, five-point, calibrations were performed: three prior to the collection of data and three following. (The lone exception to this was September 10, when only three calibrations were performed due to inclement weather and shortened monitoring day.) Response factors were determined for two isotopes of chlorine at masses 70 and 72. The average of the daily response factors (normally n = 6) was used to quantitate the days monitoring results. The relative deviation from the

daily average response factors ranged from 3% to 22% depending on the particular monitoring day. The response of the TAGA to chlorine is virtually linear over a concentration range spanning two orders of magnitude. Correlation coefficients were better than .9989 for all calibration curves over the concentration range of 10 to 900 ug/m^3.

Figure 1 is an example of a typical calibration curve for Cl_2 obtained with the mobile TAGA system in Cornwall. For this survey the detection limit for chlorine was determined to be 1 ug/m^3.

2.2.2 Chlorine Dioxide Calibration Technique

In order to calibrate the TAGA response to gaseous ClO_2, a ClO_2 gas generator was developed by this laboratory. The design of the ClO_2 generator was based on the $Cl_2/NaClO_2$ method provided in the "NCASI Technical Bulletin No. 409, September 1983". See Figure 2 for a schematic of the ClO_2 generator/ calibration system. Briefly, a certified standard of 51.7 ppm chlorine in ultra pure nitrogen supplied chlorine to an impinger, which contained aqueous chlorite. The reaction of the chlorine with the aqueous chlorite produced gaseous chlorine dioxide, which was then added to the TAGA ambient air inlet system. The generator produced ClO_2 in N_2 at a nominal concentration of 65 ppm.

Primary calibration of the ClO_2 generator was accomplished by the well-known dual pH iodometric procedure. This technique involved the immediate entrapment of the ClO_2 from the generator outlet with a neutral iodine solution, followed by a titration of the

iodine with aqueous sodium thiosulphate. Using the TAGA as a detector, it was confirmed that the ClO_2 generation gas was free of Cl_2. Final ClO_2 levels entering the TAGA ion source were regulated by simply varying the flow rates through the ClO_2 generator. The linearity of response was tested and proven to a concentration of 300 ug/m^3 (corr. coeff > 0.9984). The TAGA's detection limit for ClO_2 was determined to be 0.2 ug/m^3. The in-field calibration for ClO_2 was conducted on September 9, 1986. For all other monitoring days, the response factor of the ClO_2 was scaled to the daily chlorine calibrations.

3.0 Results and Discussion

3.1 C.I.L.

Mobile air monitoring for atmospheric Cl_2 and ClO_2 downwind of C.I.L. was conducted on September 3 and September 9, 1986. The results of all (7) monitoring periods are presented in Table 1. These results were acquired at sampling locations A and Q shown in Figure 3. Note that at the time of sampling, the TAGA was downwind of C.I.L. and upwind of Domtar. As shown in Table 1 neither Cl_2 nor ClO_2 were detected downwind of C.I.L. for any of the seven sampling periods. It is noteworthy that no chlorine-like odours were detected downwind of C.I.L. during this survey.

3.2 Domtar

In contrast to the C.I.L. results, monitoring conducted downwind of Domtar was more eventful, thus the reason for extra sampling performed downwind of Domtar. Mobile TAGA analysis of the ambient air downwind of Domtar of the target pollutants, Cl_2 and ClO_2, was conducted on September 4, 8, 9,

10, 15, 16, and 17, 1986. A total of 37 ½-hour average concentrations for Cl_2 and ClO_2 were acquired downwind of Domtar.

The ambient levels of Cl_2 and ClO_2 are provided in Table 2 along with a summary of the meteorological conditions acquired at the sampling locations and comments regarding the occurrence of odours. Again sampling locations are shown in Figure 3. (Since C.I.L. was not considered a source for detectable levels of either Cl_2 or ClO_2, all sampling locations were considered solely downwind of Domtar, including locations D and E.)

It should be noted that for most monitoring periods sulfurous odours were obvious and despite the presence of such odours, chlorine-like odours were frequently noted, particularly at locations directly downwind of Domtar on Brookdale Avenue.

3.2.1 ClO_2 (Domtar)

The ambient levels of gaseous ClO_2 recorded by the TAGA downwind of Domtar range from ND (not detected above 0.2 ug/m^3) to 17 ug/m^3. The highest ½-hour average concentration was 17 ug/m^3 (sample D12) at location B on September 9 between 18:18 and 18:48 hours. However, this was the only reading above 10 ug/m^3. In fact, 20 of 37 ½-hour average concentrations were below 1 ug/m^3. The Ministry standard of 85 ug/m^3 for a ½-hour average concentration was not exceeded for any of the 37 monitoring periods.

3.2.2 Cl_2 (Domtar)

Simultaneous with the measurement of ClO_2, the TAGA unit recorded the ambient levels of Cl_2 downwind

of Domtar. As shown in Table 2 the ½-hour average concentration range from 4.4 ug/m³ to 840 ug/m³. The distribution of Cl_2 concentration ranges recorded downwind of Domtar is depicted by a frequency plot given by Figure 4. Twenty-four (24) of the 37 ½-hour sampling periods indicate Cl_2 concentrations greater than 100 ug/m³ for a ½-hour average. More importantly, 27% (10 of 37) of the readings were greater than the Ministry standard of 300 ug/m³ for a ½-hour average concentration. While 7 of the ½-hour average Cl_2 concentrations were more than twice the Ministry standard, that is, greater than 600 ug/m³.

The Cl_2 monitoring results of Table 2 are plotted on an area map in Figure 5. As clearly shown, the highest levels of Cl_2 (samples D1, D9-D12, D21, D34-D37) were recorded on Second Avenue, west of Brookdale Avenue at locations A, B, J, I, and R. For those periods when the Cl_2 levels exceeded the Ministry standard our sampling locations were downwind of Domtar and upwind of C.I.L.

Figure 5 also shows that ambient Cl_2 levels were much lower at distances a few hundred meters from the Domtar property line. Chlorine levels in the residential areas east of Brookdale Avenue were well below the Ministry standard of 300 ug/m³.

TABLE 1: Summary of Results - Mobile TAGA Survey: Cornwall (1986)
Ambient Levels of Cl_2 and ClO_2 Downwind of C.I.L.

Sample No.	Date	Monitoring Period	Location	Met. Con. AT	WS	WD	Concentration (ug/m^3) Cl_2	ClO_2	±%	Comments
C1	3/9	12:51-13:21	A	20	5-15	NE	ND	ND	17	no odours
C2	3/9	13:21-13:51	A	20	5-15	NE	ND	ND	17	no odours
C3	3/9	13:51-14:21	A	20	5-15	NE	ND	ND	17	no odours
C4	3/9	14:35-15:05	A	20	5-15	NE	ND	ND	17	no odours
C5	16/9	12:59-13:29	Q	13	10-30	NNW	ND	ND	16	no odours
C6	16/9	13:29-13:59	Q	13	10-25	NNW	ND	ND	16	no odours
C7	16/9	13:59-14:29	Q	13	10-20	NNW	ND	ND	16	no odours

Note 1 See Figure 3 for monitoring locations
2 AT = ambient temperature (°C); WS = range of wind speeds (km/hr); WD = predominant wind direction
3 ND = below detection limits; 1 ug/m^3 (Cl_2); 0.2 ug/m^3 (ClO_2)
4 ±% uncertainty based on multiple daily calibrations of Cl_2

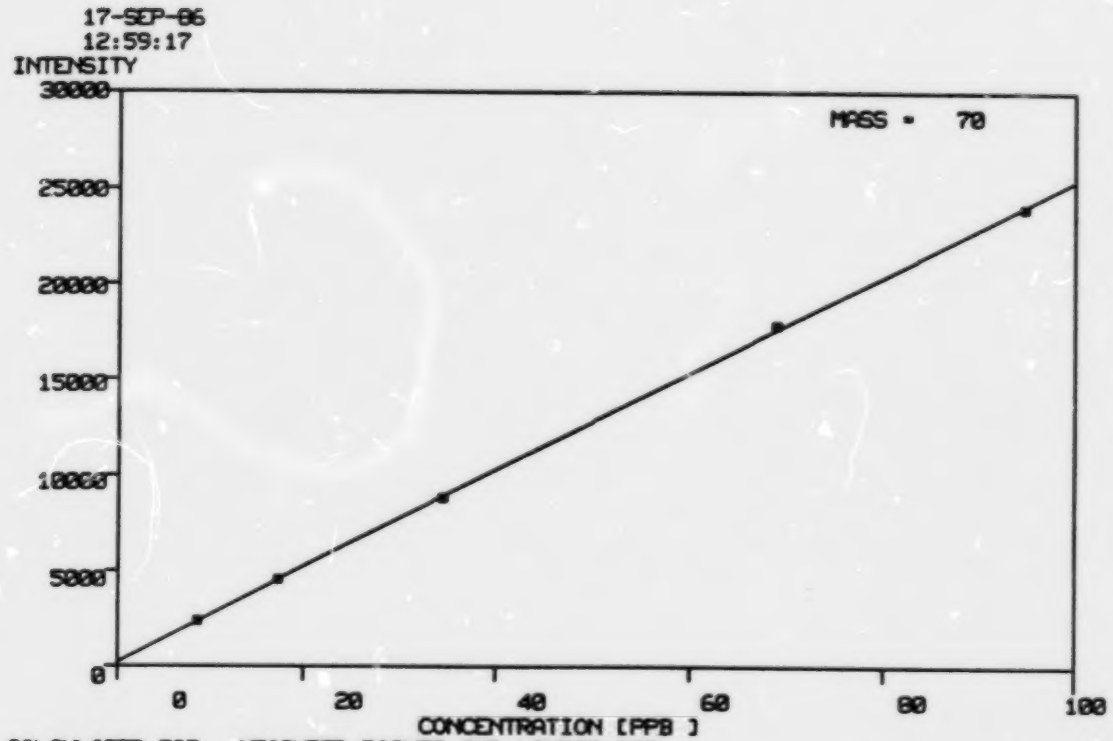
TABLE 2: Summary of Results - Mobile TAGA Survey: Cornwall (1986)
Ambient Levels of Cl_2 and ClO_2 Downwind of Domtar

Sample No.	Date	Monitoring Period	Location	Met. Con. AT	WS	WD	Concentration (ug/m^3) Cl_2	ClO_2	±%	Comments
D1	4/9	9:19- 9:49	A	22	5-10	SE	640	.58	10	strong TRS/Cl_2 odours
D2	4/9	10:54-11:24	B	23	0- 5	W	230	ND	10	variable light winds, strong odours
D3	4/9	11:39-12:09	C	26	0-10	SE	100	ND	10	moderate TRS/Cl_2 odours
D4	4/9	12:09-12:39	C	25	5-15	SE	17	ND	10	light TRS/Cl_2 odours
D5	4/9	14:22-14:52	D	25	10-20	SSW	29	ND	10	light TRS/Cl_2 odours
D6	4/9	14:52-15:22	D	25	15-25	SSW	32	ND	10	light TRS/Cl_2 odours
D7	4/9	15:22-15:52	D	25	15-25	SSW	55	ND	10	light TRS/Cl_2 odours
D8	4/9	15:52-16:22	D	25	15-25	S	39	ND	10	light TRS/Cl_2 odours
D9	4/9	16:42-17:12	B	23	10-15	SSE	840	3.7	10	strong TRS/Cl_2 odours
D10	4/9	17:12-17:42	B	22	10-20	SSE	800	8.6	10	strong TRS/Cl_2 odours
D11	4/9	17:48-18:18	B	22	10-15	SSE	630	9.8	10	strong TRS/Cl_2 odours
D12	4/9	18:18-18:48	B	22	10-15	SSE	630	17	10	strong TRS/Cl_2 odours
D13	4/9	20:14-20:44	E	20	15-25	S	160	2.0	10	strong TRS/Cl_2 odours
D14	8/9	14:27-14:57	F	17	15-30	W	130	ND	19	strong TRS odours
D15	8/9	15:05-15:35	G	18	10-25	WSW	130	ND	19	strong TRS odours
D16	8/9	15:35-16:05	G	18	15-25	W	110	ND	19	strong TRS odours
D17	8/9	16:45-17:15	H	17	10-25	WSW	190	ND	19	moderate TRS/Cl_2 odours
D18	8/9	17:16-17:46	H	17	15-25	WSW	210	0.23	19	variable winds, moderate odours
D19	8/9	17:54-18:24	I	17	15-25	SW	270	1.2	19	variable winds, moderate odours
D20	8/9	18:24-18:54	I	16	15-25	SW	140	0.49	19	variable winds

TABLE 2 (Cont'd)

Sample No.	Date	Monitoring Period	Location	Met. Con. AT	WS	WD	Concentration (ug/m^3) Cl_2	ClO_2	±%	Comments
D21	8/9	19:06-19:36	J	15	10-15	SW	510	6.5	19	strong TRS/Cl_2 odours
D22	8/9	19:37-20:07	J	14	10-15	SSW	250	4.2	19	variable winds, odours
D23	9/9	14:53-15:23	I	22	15-30	WSW	130	0.45	9	moderate TRS/Cl_2 odours
D24	9/9	15:27-15:57	I	22	15-30	WSW	170	0.38	9	moderate TRS/Cl_2 odours
D25	9/9	16:14-16:44	K	23	15-25	WSW	55	ND	9	wind shift after 20 minutes
D26	9/9	16:54-17:24	L	22	10-25	WSW	20	ND	9	
D27	10/9	8:43- 9:13	A	15	0- 3	E	84	0.20	3	winds too light, rain
D28	15/9	14:14-14:44	M	14	15-30	WSW	4.4	ND	22	light TRS odours
D29	15/9	15:03-15:33	N	17	10-20	WNW	12	ND	22	light TRS odours
D30	15/9	15:47-16:17	O	15	5-15	W	31	ND	22	light TRS odours
D31	16/9	11:41-12:11	P	11	5-20	NNW	14	ND	16	variable winds, brief TRS odours
D32	16/9	12:11-12:41	P	12	10-20	NNW	14	ND	16	variable winds, brief TRS odours
D33	17/9	13:45-14:15	I	16	0-15	WSW	185	ND	5	strong TRS odours
D34	17/9	14:16-14:46	I	15	5-15	SW	630	0.30	5	strong TRS/Cl_2 odours
D35	17/9	15:01-15:31	R	16	5-15	SW	680	0.29	5	strong TRS/Cl_2 odours
D36	17/9	15:32-16:02	R	16	5-15	SW	590	0.25	5	strong TRS/Cl_2 odours
D37	17/9	16:03-16:33	R	17	5-15	SW	430	0.2	5	strong TRS/Cl_2 odours

Note 1 See Figure 3 for monitoring locations
2 AT = ambient temperature (°C); WS = range of wind speeds (km/hr); WD = predominant wind direction
3 ND = below detection limits; 1 ug/m^3 (Cl_2); 0.2 ug/m^3 (ClO_2)
4 ±% uncertainty based on multiple daily calibrations of Cl_2



CALCULATED FIT - MEASURED POINTS AND LINEAR FIT
CALIBRATION FOR CL2

LEAST SQUARES LINEAR REGRESSION RESULTS

MASS	N	SLOPE	INTERCEPT	R2
70.0	5.	252.5916	193.5872	0.9999
72.0	5.	151.6148	107.5903	0.9999

FIGURE 1: EXAMPLE OF A CHLORINE CALIBRATION (TAGA)
CORNWALL SURVEY
SEPTEMBER, 1986

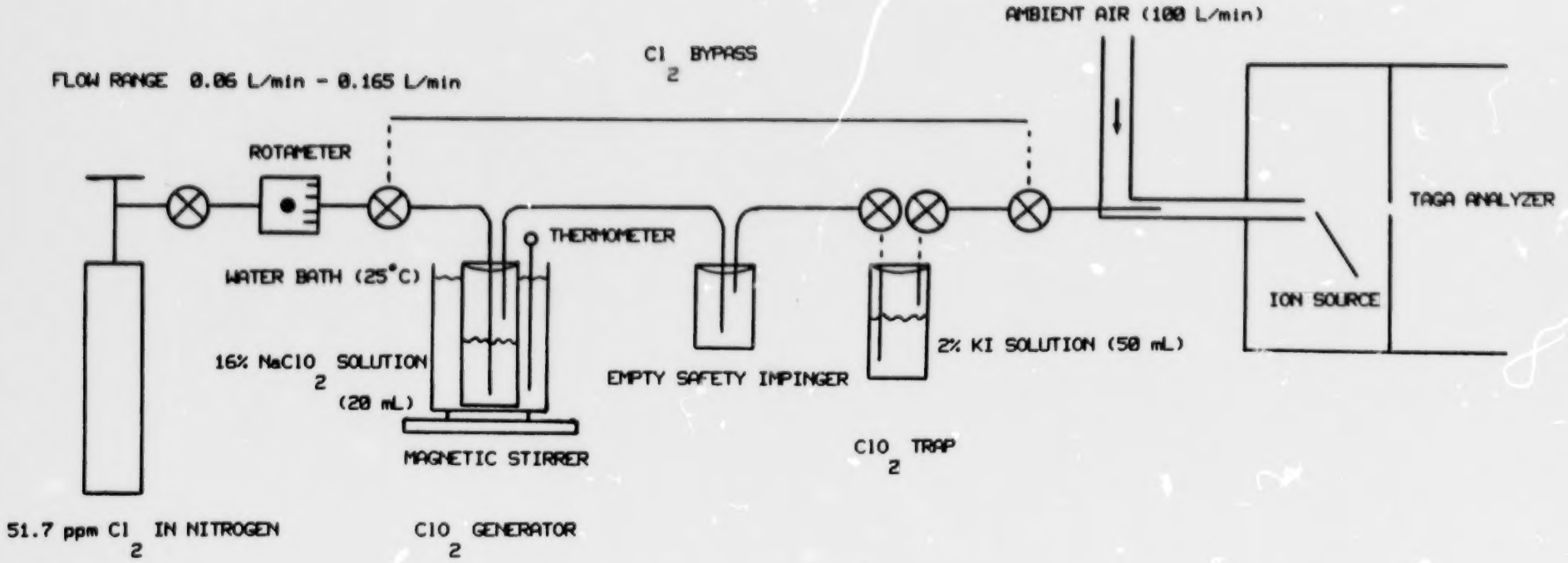


FIGURE 2: SCHEMATIC OF CHLORINE DIOXIDE GENERATOR, CHLORINE AND CHLORINE DIOXIDE CALIBRATION SYSTEM.

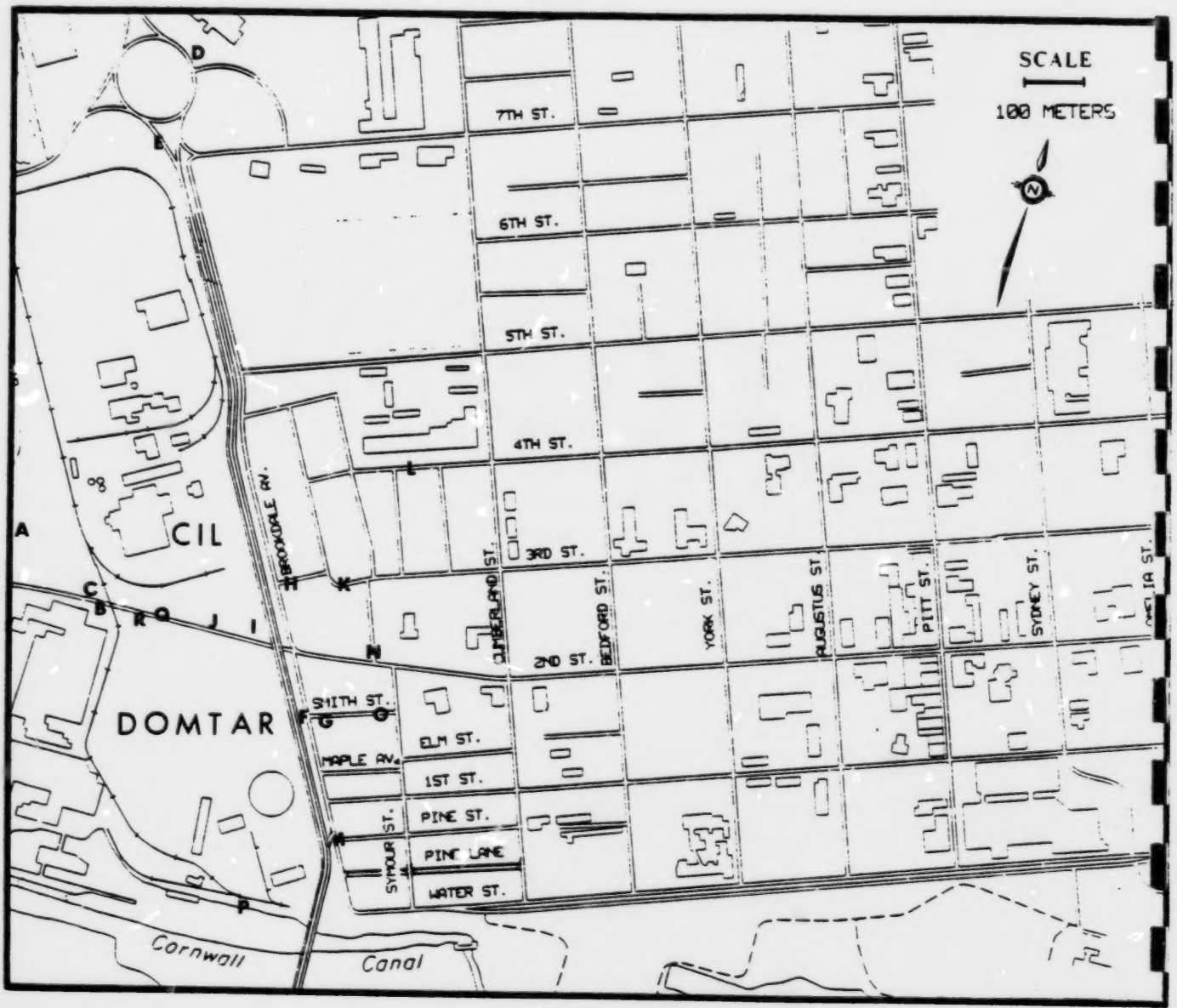


FIGURE 3: MONITORING LOCATIONS
CORNWALL SURVEY
SEPTEMBER, 1986.

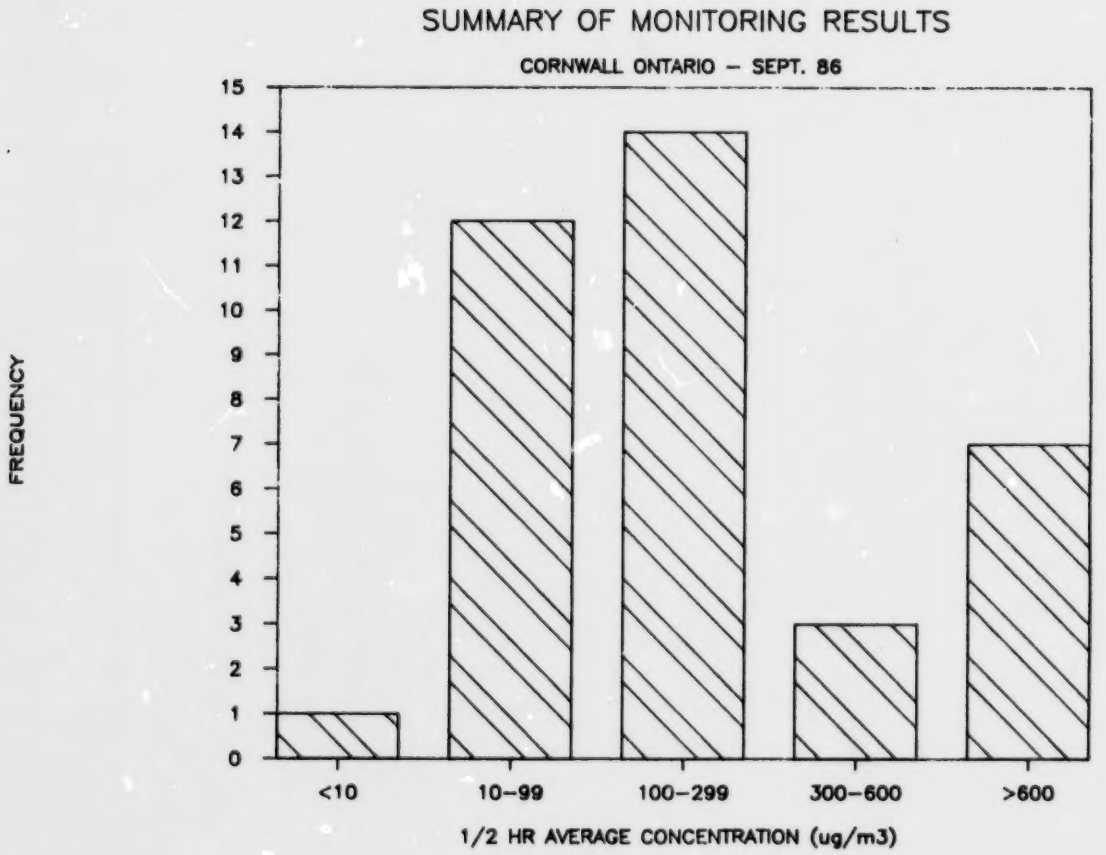


FIGURE 4: CHLORINE CONCENTRATIONS
DOWNWIND OF DOMTAR
CORNWALL SURVEY
SEPTEMBER, 1986

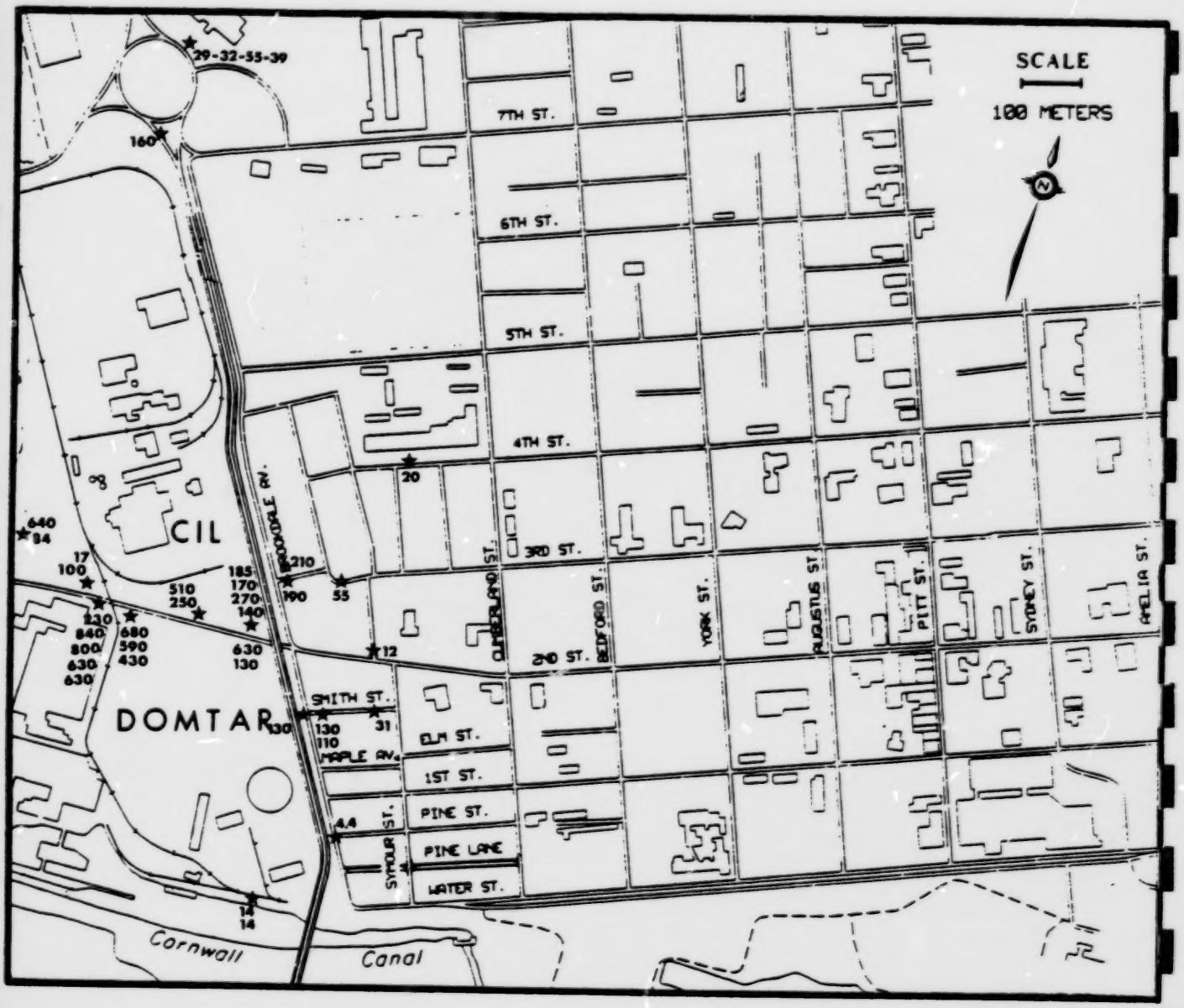


FIGURE 5: 1/2-HOUR AVERAGE CONCENTRATIONS OF CHLORINE RECORDED DOWNWIND OF DOMTAR CORNWALL SURVEY SEPTEMBER, 1986.